Buckner

The Development Of A Hard Boro-Silicate Glaze For American Porcelain

THE DEVELOPMENT OF A HARD BORO-SILICATE GLAZE FOR AMERICAN PORCELAIN

BY

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THESIS

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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ENTITLED The Development of a Hard Boro-Silicate Glaze for American Porcelain

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

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A Hard Boro-Silicate Glaze for American Porcelain at Cone 6.

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I. The Object of the Investigation.

American porcelain is glazed at a much lower temperature than the European porcelain. The glazes employed are the same as are used on whiteware, viz., borosilicates of lead, calcium, the alkalies, and aluminium. A good glaze of this type possesses high brilliancy, an excellent surface texture, low viscosity, and a comparatively long range of fusion.

Owing to the fact that American manufacturers biscuit their ware at a high temperature, glazes of the true porcelain type are not used. The cost and danger of loss from warping and deformation of the body make two successive burnings at cone 8 or higher, prohibitory. In Europe on the other hand, porcelain is biscuited at a low temperature, approximately 1100°C, and leadless glazes maturing from cone 8 to cone 15 can be used. These glazes lack the high gloss and smooth surface texture possessed by those of the whiteware type but have the great advantage of being materially harder. The relative softness of the latter type may be considered a serious defect inasmuch as American porcelain is easily marked with cutlery. It is not an uncommon sight to see plates and similar articles of American manufacture covered with hundreds of small scratches.

The principal object of this work has been to develop a glaze which would be harder and more resistant to abrasion than those now used and yet be adaptable to the American methods of manufacture.

To accomplish this purpose it was necessary to resort to a higher maturing temperature in order to eliminate some of the softer silicates. A temperature of 1140°C, corresponding approximately to cone 6 was thought to be as high as it was feasible to go. At this temperature some of the softer silicates which impart high gloss and low viscosity to a glaze, can be retained and losses from undue softening of the ware would be unlikely.

II. Description of the Work.

(1) Requirements to be met.

Any substitute for the ordinary whiteware glaze should meet the fol-

lowing requirements:

(a) It should have as pleasing an appearance as regards color, gloss, and surface texture as those now used.

(b) It should have a sufficient temperature range to make possible the production of as good ware in the top as in the bottom of the ordinary potter's kiln.

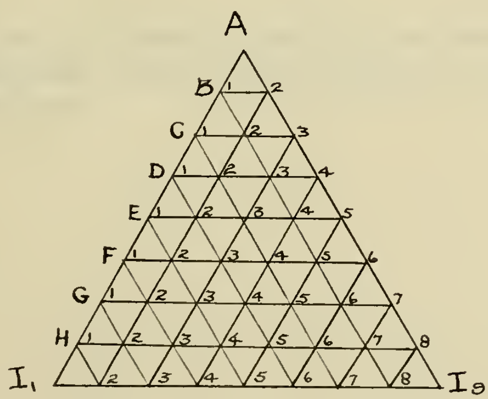
(c) It should permit the use of underglaze colors.

(d) In order to justify its use, it should be considerably harder and less subject to abrasion than the present type of glaze.

(2) Method of Procedure.

By blending a characteristic whiteware glaze with the true porcelain and leadless boric-acid types, it was thought that a glaze could be produced which would be materially harder than the former but which would still retain some of its desirable properties.

The range of composition was made sufficiently large to determine by means of hardness tests, the relations of increasing alumina and silica and decreasing boric acid and lead to the hardness of the respective glazes. The following group was prepared:



A. $\left.\begin{matrix} .3 & K_2O \\ .7 & CaO \end{matrix}\right)$ $.5\ Al_2O_3 \quad 4\ SiO_2$

I_1 $\left.\begin{matrix} .064 & K_2O \\ .192 & Na_2O \\ .49 & CaO \\ .25 & PbO \end{matrix}\right)$ $\left.\begin{matrix} .3\ Al_2O_3 \\ .2\ B_2O_3 \end{matrix}\right\}$ $3.0\ SiO_2$

I_9 $\left.\begin{matrix} .02 & K_2O \\ .1 & MgO \\ .65 & CaO \\ .05 & ZnO \end{matrix}\right\}$ $\left.\begin{matrix} .28\ Al_2O_3 \\ .2\ B_2O_3 \end{matrix}\right\}$ $3.0\ SiO_2$

To further aid in the selecting of the best type glaze from this group, all glazes were tested over six standard underglaze colors.

Bulletin No.21 - Bureau of Domestic and Foreign Commerce. Slight changes have been made in these glazes to raise the maturing temperature.

(3). Preparation of Frits and Glazes.

The frit batches recuired were thoroughly mixed and fused in a small drop-frit furnace after which they were finely ground in ball mills with the requisite amount of water for about two hours. The batch weights for the frits and corner glazes of Group I. are given in Table I.

TABLE I.

	Frit Mixtures		Glaze Mixtures		
Glaze Number	I_1	I_9	I_1	I_9	A
Potassium feldspor	55.6	55.6	7.78	83.4	166.8
Borax	76.4				
Red lead	114.0				
Whiting	20.0		39.0	35.0	70
Flint	72.0	60.0	70.5	62.4	108
Magnesium carbonate		72.0			
Boric Acid		16.8			
Zinc oxide		49.6			
Frit		8.1	145.35	102.65	70
China Clay			37.1	20.6	
Soda feldspor			48.2		

(4) Under Glaze Colors.

Six standard underglaze colors of the composition given below were used. These mixtures were calcined at cone 12 and after thorough grinding were washed several times to free them from soluble salts. They were then painted on the test pieces in small lines before applying the glaze.

Pink: Per Cent.

SnO_2	50.0
$CaCO_3$	25.0
SiO_2	18.0
$K_2Cr_2O_7$	3.0
$Na_2O.2B_2O_3 10H_2O$	4.0
	100.0

Victoria Green:

Cr_2O_3	50.0
flux	50.0

Flux

SiO_2	30
$K_2Cr_2O_7$	6.0
PbO	3.0
$CaCO_3$	3.0
KNO_3	1.0

Yellow

Al_2O_3	8.0
SnO_2	16.0
Sb_2O_3	32.0
Pb_3O_4	44.0

Blue Green

Cr_2O_3	20.0
Co_2O_3	5.0
China Clay	27.5
Feldspor	27.5
ZnO	20.0

Brown

Fe_2O_3	18.0
Cr_2O_3	17.0
Al_2O_3	11.5
ZnO	53.5
	100.0

Blue

Co_2O_3	44.5
Al_2O_3	55.5

(5) Trial Pieces

For the trial pieces a body of the following composition, biscuited at Cone 12, was used.

23.0% Brandywine Summit Feldspor

28.5 Silica

38.5 North Carolina Kaolin

9.5 Tenn. ball Clay No.7

0.5 Whiting

The body mixture was first ground wet for a short time in ball mills, then dried out in plaster molds to a stiff mud consistency.

Two forms of test pieces were prepared: round disks, approximately 6.5 cm. in diameter by 1 cm. thick, for use in the abrasion test, and oblong tiles 2½ inches long by 1½ inches wide, for testing the action of the glazes on the underglaze colors. They were pressed by hand in brass molds.

(6) Firing of Glazes.

All glazed test pieces were burned in closed saggers, the disks used for the abrasion test being set on edge and supported with strips of fire clay. Group I was burned in a coal fired test kiln to cone 6 in about 24 hours while series 2 and series 3 were burned in an open fire gas kiln in about the same length of time.

(7) Methods Used for Testing Hardness.

The Sclerometer.

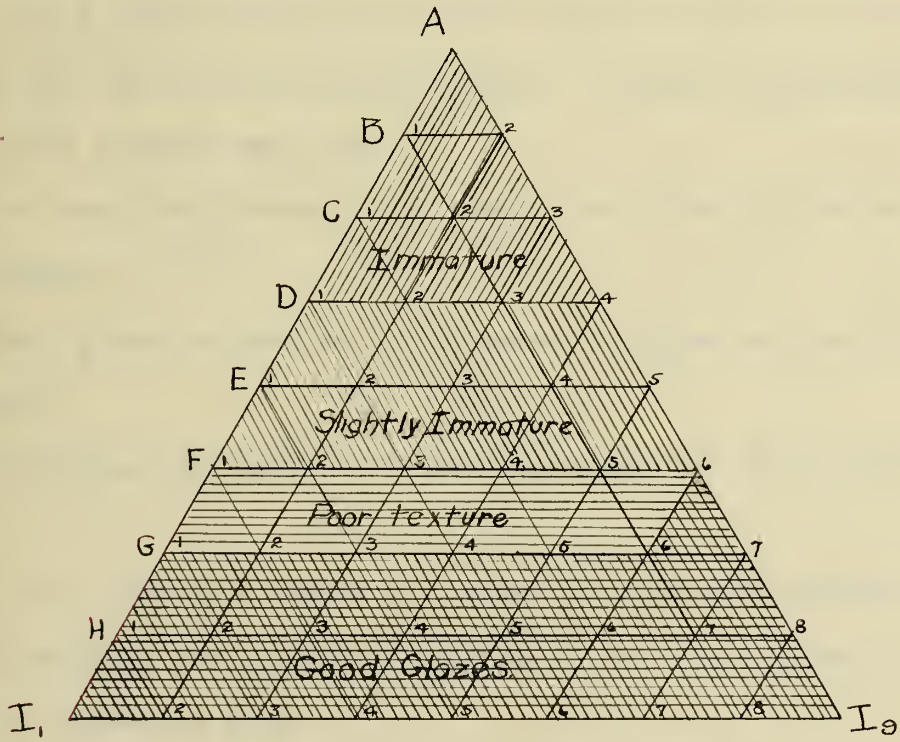
The hardness of the glazes in Group I. was tested by means of a sclerometer which consists principally of a weighted needle or point of either steel or diamond below which is a car to which the sample to be tested is fastened. The test piece can be scratched by drawing the car beneath the point. Either the weight required to draw the car beneath the point or the size of the scratch produced by a definite weight upon the needle may be taken as a measure of the hardness. Obviously the instrument is only used to determine the relative hardness of a number of samples. In this work the diamond point was loaded down with a 500 gm. weight and the widths of the scratches produced upon the glazes were measured by means of a micrometer microscope. Each piece was scratched several times and the average width of the scratches determined.

Abrasion Test.

As a check on the sclerometer test the glazes were subjected to an abrasion test. Round porcelain disks, approximately 8.6 cm. in diameter and 1.0 cm. thick, were glazed on both sides, placed in ball mills, and abraded with sand. Two disks at a time were placed in the mills with 4 lbs. of clean, white silica sand and the latter rotated for a period of 3 hours. The mills were porcelain lined, $9\frac{3}{4}$" in diameter by 13" long, and rotated at the rate of 160 R. p.m. Since the disks were glazed on both sides the loss in weight per 2 sq. cm. of glazed surface was taken as a measure of the hardness.

RESULTS

Appearance and Condition of Glazes of Group I.



Group I. (continued)

The glazes from A to D were very immature.

The glazes from E_1 to E_5 were slightly immature and contained many small, enclosed bubbles. The surface texture was rough and unpleasing in appearance.

The glazes from F_1 to F_6 were slightly immature and contained many enclosed bubbles but the surface textures of all were slightly better than in glazes E_1 to E_5

Glazes G_1, G_2, and G_3, contained enclosed bubbles and their surface textures were poor.

Glazes G_4 to G_6 contained very few bubbles and their surface textures were slightly better than G_1 or G_2.

$Glaze_7$ contained no enclosed bubbles, its color was good but its gloss and surface texture were only fair.

Glazes H_1 and H_2 had excellent gloss and texture but were not very white.

Glazes H_3, H_4, and H_5 were all good glazes. The color was white and the gloss and surface textures were fair.

Glaze I_1 was excellent in respect to texture and gloss but the color was slightly yellowish.

Glaze I_2 and I_3 were as good as I_1 in respect to gloss and texture and were whiter in color.

I_4 was a good glaze in regard to texture and color but did not show as high gloss as I_1

Glazes I_5 to I_8 were good glazes but lacked the high gloss possessed by I_1.

Glaze I_9. The glaze was applied too thickly on the trial piece and showed slight opacity around the edges.

The Effect on Underglaze Colors.

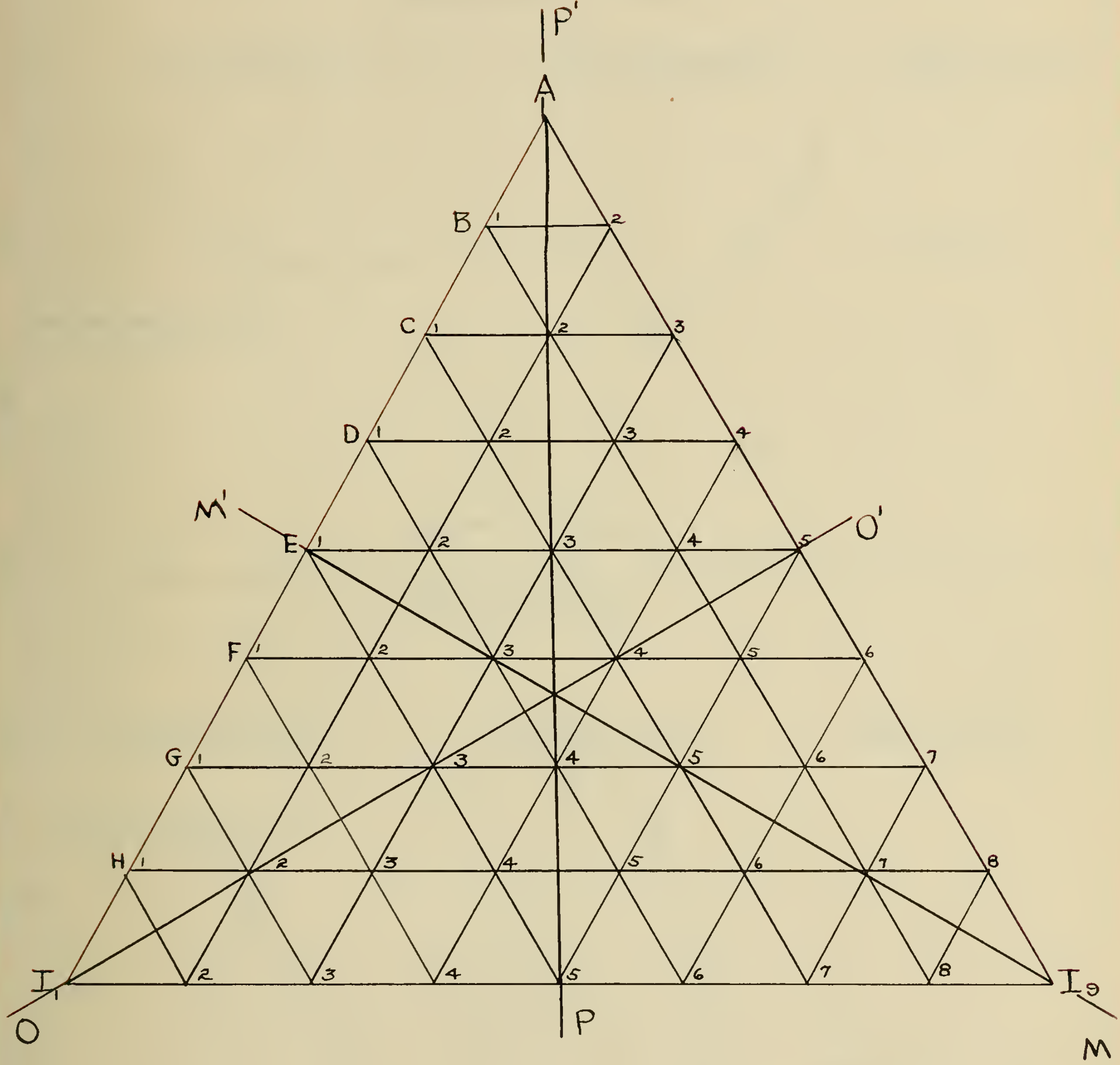
As a whole the mature glazes in this group had a deleterious effect on underglaze colors. The pink was destroyed in all cases except in glazes E_2

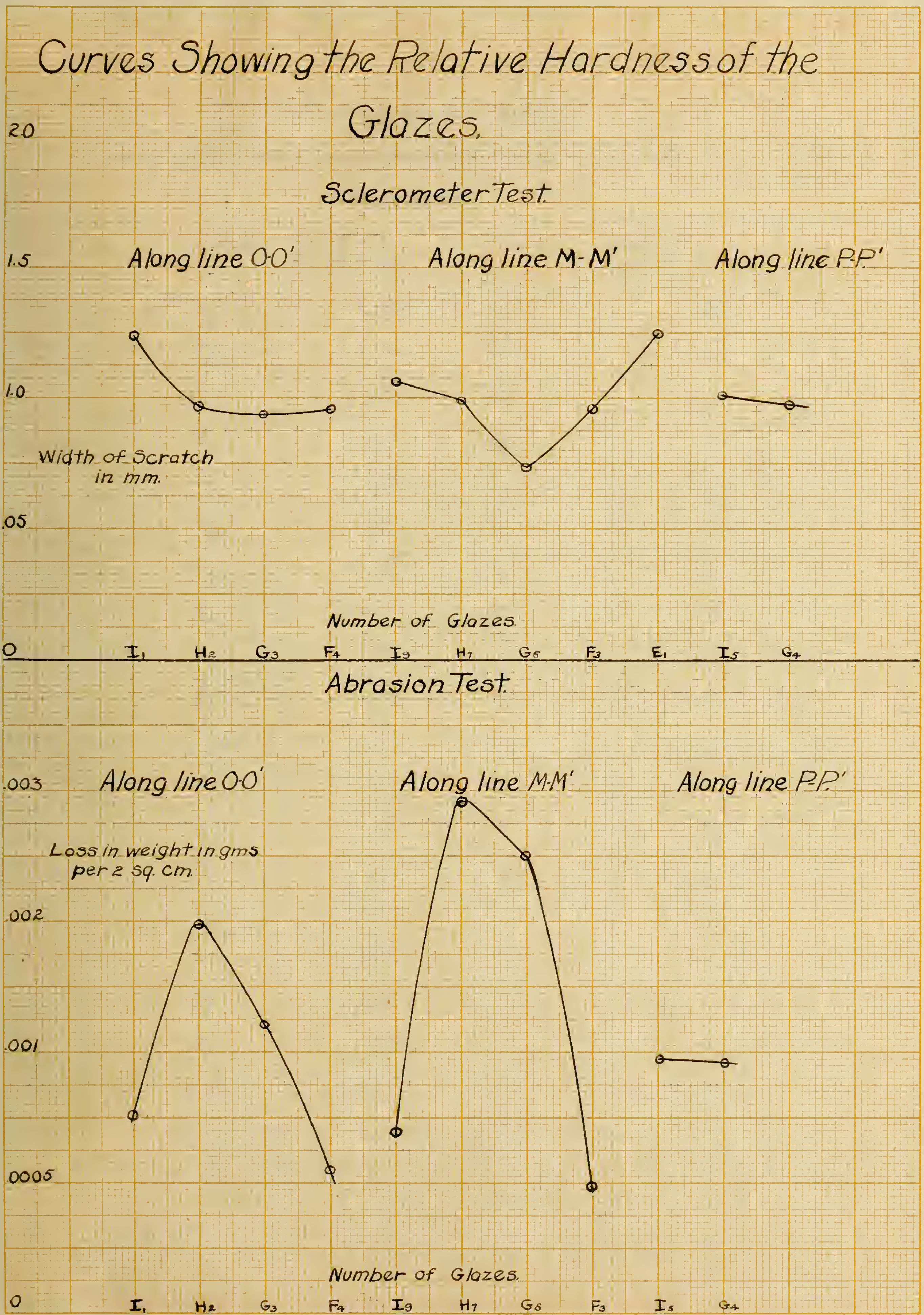
and F_6.

In series I_1 and I_8 the blue and brown colors flowed, and in glazes I_5 - I_9 of this series the green color was changed to a lighter shade.

In series H_1 - H_8 the blue and brown colors flowed slightly. The green was changed to an olive color in all but glazes H_1 and H_2.

The remainder of the mature glazes had a similar destructive effect on these colors with the exception of glazes F_2, F_5, and F_6 in which the colors were all good with the exception of the pink.


P'
A
B
C
D
E
F
G
H
I_1
I_9
M'
O'
O
M
P



Curves Showing the Relative Hardness of the Glazes.
Sclerometer Test.
Along line O-O'
Along line M-M'
Along line P-P'
2.0
1.5
1.0
.05
0
Width of Scratch in mm.
Number of Glazes.
I1 H2 G3 F4 I9 H7 G5 F3 E1 I5 G4
Abrasion Test.
Along line O-O'
Along line M-M'
Along line P-P'
Loss in weight in gms per 2 sq. cm.
.003
.002
.001
.0005
0
Number of Glazes.
I1 H2 G3 F4 I9 H7 G6 F3 I5 G4

Results of Tests for Hardness.

Only mature and slightly immature glazes were tested.

Sclerometer.

Glaze	Width of Scratch mm.	Glaze	Width of Scratch in mm.
E_1	1.24	H_3	.99
E_2	1.16	H_4	.88
E_3	.93	H_5	1.05
F_1	.76	H_6	.98
F_2	.92	H_7	.99
F_3	.94	H_8	.92
F_4	.93	I_1	1.24
F_5	.79	I_2	1.25
F_6	.94	I_3	1.08
G_1	.99	I_4	1.16
G_2	.87	I_5	1.03
G_3	.89	I_6	1.10
G_4	.96	I_7	1.07
G_5	.72	I_8	1.11
G_6	1.12	I_9	1.12
G_7	1.01		
H_1	1.13		
H_2	.95		

Abrasion Test

No.	wt. glazed	wt. after abrasion	area sq. cm.	loss	loss per 2 sq.cm.
F(1)	134.00	133.74	233	.26	.0011
F(2)	142.47	142.23	231	.24	.0011
F(3)	142.82	142.71	225	.11	.00048
F(4)	145.21	145.09	235	.12	.00051
F(5)	133.6	133.49	228	.11	.00044
F(6)	142.17	141.99	233	.18	.00077
G(1)	161.68	161.22	225	.46	.0022
G(2)	173.0	172.78	228	.22	.00096
G(3)	150.89	150.62	226	.27	.0012
G(4)	170.39	170.17	237	.22	.00093
G(5)	164.62	164.00	241	.62	.0025
G(6)	158.66	158.44	228	.22	.00095
G(7)	154.79	154.44	224	.25	.0011
H(1)	166.09	159.49	232	.60	.0026
H(2)	154.2	153.77	229	.43	.0019
H(3)	147.68	147.36	232	.32	.0014
H(4)	166.70	166.55	229	.15	.00066
H(5)	149.27	148.87	226	.40	.0018
H(6)	149.00	148.89	228	.11	.00048
H(7)	160.59	159.88	243	.71	.00292
H(8)	152.91	152.45	330	.46	.00200
I(1)	166.48	166.30	233	.18	.00077
I(2)	153.49	153.02	226	.47	.00208
I(3)	166.10	165.84	231	.26	.00112
I(4)	149.24	148.94	231	.30	.00130
I(5)	154.22	153.99	239	.23	.0095
I(6)	149.76	149.33	226	.43	.00190
I(7)	151.72	151.26	230	.46	.00200
I(8)	160.17	159.81	240	.36	.0015
I(9)	164.91	164.79	222	.12	.00054

Series II.

The hardness tests showed that hardness increased with increasing silica and alumina and decreasing boric acid. By reference to Group I. it will be seen that series G_1 - G_7, on the whole, is the hardest of the mature series. The lead content of these glazes decreases from G_1 to G_7.

It has recently been reported that leadless boric-acid glazes are impractical at the present day for American porcelain since the short maturing

E. T. Montgomery: Technologic Paper No.31, Bureau of Standards.

range of temperature of such glazes causes a considerable loss through the production of "seconds" in the colder portions of the potter's kiln. Consequently it was decided to improve glaze G_3 containing as shown below, sufficient lead to produce lower viscosity than possessed by a similar type of leadless glaze. This improvement was brought about by replacing lime in the RO with strontium. The following series was designed:-

$$G_3 \quad \left.\begin{array}{l} .096\ Na_2O \\ .158\ K_2O \\ .025\ MgO \\ .5825\ CaO \\ .125\ PbO \\ .0125\ ZnO \end{array}\right) \left.\begin{array}{l} .345\ Al_2O_3 \\ .15\ B_2O_3 \end{array}\right) 3.25\ SiO_2$$

$$G_3\text{-}15 \quad \left.\begin{array}{l} .096\ Na_2O \\ .156\ K_2O \\ .025\ MgO \\ .4325\ CaO \\ .125\ Pbo \\ .0125\ Zno \\ .15\ Sro \end{array}\right) \left.\begin{array}{l} .345\ Al_2O \\ .15\ B_2O_3 \end{array}\right) \quad 3.25\ SiO_2$$

Equivalent of Sro replacing CaO

G_3 ——————————— G_3 -15
0 03 06 09 12

TABLE IV.

Glazes and Frits Used in Series 2 and Series 3.

Glaze Number	Frit Mixtures G_3	G_3 -.15	H_4	H_4-.15	Glaze Mixtures G_3	G_3-.15	H_4	H_4-.15
Potassium feldspar			55.6		88	87.8	24.7	73.1
Red lead	57.0	57.0	57.0	57.0				
lime stone	55.8	35.8	45.8	25.8	30.35	60.9	24.75	29.75
borax	57.3	57.3	66.8	66.8				
sodium carbonate	4.44	4.44	1.8	1.8				
flint	84	108	72.0	108	60.5	123.2	78.7	60.7
frit					124.97	129.775	101.1	133.95
Magnesium carbonate					2.1	4.20	3.15	3.15
Zinc-oxide					1.02	2.04	1.51	1.51
China clay		25.8		25.8	35.7	70.6	66.6	31.7
Strontium oxide		31.2		31.2				

RESULTS

Series II.

Burned at Cone 6..

Glaze G_3 contained a few bubbles. The texture and gloss were poor.

Glaze G_3-03 showed no evidence of bubbling. The texture and gloss were much improved but were only fair in quality.

Glaze G_3-06 was the same as G_3-03.

Glazes G_3-09, G_3-12 and G_3-15 showed no improvement over G_3-03.

Four of the underglaze colors were bright and unaffected. The pink, however, was entirely destroyed and the green was changed to an olive color.

Series III.

Due to the fact that the glazes obtained in Series II were not entirely satis-

factory, the lime in glaze H_4 was replaced by stronium -oxide . This glaze, originally, was superior in gloss and surface texture to Glaze G_3.

$$H_4 \quad \left.\begin{array}{l} .096\ Na_2O \\ .1445\ K_2O \\ .5775\ CaO \\ .125\ PbO \\ .0375\ MgO \\ .0187\ ZnO \end{array}\right) \left.\begin{array}{l} .3175\ Al_2O_3 \\ .175\ B_2O_3 \end{array}\right) 3.125\ SiO_2$$

$$H_4\text{-}15 \quad \left.\begin{array}{l} .096\ Na_2O \\ .1445\ K_2O \\ .4275\ CaO \\ .125\ PbO \\ .0375\ MgO \\ .0187\ ZnO \\ .15\ SrO \end{array}\right) \left.\begin{array}{l} .3175\ Al_2O_3 \\ .157\ B_2O_3 \end{array}\right) 3.125\ SiO_2$$

H_4 0——.03——.06——.09——.12——H_4-15

This series was burned at cones 5, 6, and 7 to determine the maturing range of temperature of the different glazes.

Results.

At Cone 4.

Glaze H_4 was a fair glaze but the texture was a little rough.

Glaze H_4-03 was an excellent glaze with high gloss and good surface texture. The color was very white.

Glaze H_4 was the same as H_4-03.

Glaze H_4-09 was the same as H_4-03, but the color was not quite so white.

Glazes H_4-12 and H_4-15 showed no improvement over Glazes H_4-03 or H_4-06.

All of the under-glaze colors remained bright with the exception of the pink which was slightly affected.

At Cone 6.

Glaze H_4 still had a rough texture.

Glaze H_4-03 was an excellent glaze with good texture and gloss.

Glaze H_4-06 was the same as H_4-03.

Glaze H_4-09 was a good glaze but showed no improvement over H_4-03.

Glaze H_4-12 showed a poorer surface texture than H_4-09

Glaze H_4-15 was not tested.

All underglaze colors were bright and unaffected with the exception of the pink.

At Cone 7.

Glaze H_4 was a good glaze but the texture was poor.

Glaze H_4 was a much better glaze than H_4, the gloss being much improved. However, the surface was slightly eggshelled, but the appearance was not unpleasing.

Glaze H_4-06 was the same as H_4-03.

Glaze H_4-09 had an eggshelled surface or texture that was more pronounced than in H_4-03.

Glaze H_4-12 was the same as H_4-12

Glaze H_4-15 was badly crawled.

Several vases were glazed with No.H_4-03 at Cone 7. There was no flowing or noticeable deformation of the glaze. The effect on the underglaze colors was not very satisfactory at Cone 7. The brown color flowed slightly, the green was changed to a lighter shade, and the pink color was entirely destroyed.

DISCUSSION OF RESULTS

The results obtained for relative hardness of the different glazes in Group I. indicate that hardness increases with increasing alumina and silica and decreasing boric acid. The softest glazes as determined by the sclerometer were those highest in lead.

Of the two tests the sclerometer method is thought to be the better since the results obtained by it seem to be more consistent. The main difficulty with the abrasion test was the shipping of the test pieces at the edges.

In regard to fusibility, series 3 may be said to have a range of maturing temperature of at least four cones. This is sufficient to insure a small loss from over or under-burning in the lower and upper portions of the ordinary potter's kiln.

With the underglaze colors good results were obtained at cone 4 with the exception of the pink which was very slightly affected. At cone 6 the colors were bright but the pink was entirely destroyed. At cone 7, three of the underglaze colors were affected and it may be said that cone 6 is the limiting temperature at which the glazes of series 3 may be used with these standard colors.